

# Electrochemical dissolution of metallic platinum in ionic liquids

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**Abstract** The electrochemical dissolution of Pt in several ionic liquids (IL's) was studied. Different IL's were tested assessing their potential to dissolve Pt. Dissolution rate and current efficiency were evaluated. The main focus was on Cl containing IL's: first generation, eutectic based IL's and second generation IL's with discrete anions. Pt dissolution only occurred in type 1 eutectic-based IL's with a max. dissolution rate of  $192.2 \text{ g m}^{-2} \text{ h}^{-1}$  and a max. current efficiency of 99 % for the  $\text{ZnCl}_2$ -1-ethyl-3-methylimidazolium chloride IL, and  $9.090 \text{ g m}^{-2} \text{ h}^{-1}$  and 96 % for the 1:1  $\text{ZnCl}_2$ -choline chloride ionic liquid. The dissolution occurred via the formation of  $[\text{PtCl}_x]^{y-}$  complexes. To form these complexes, addition of a metal chloride was necessary. Furthermore, an IL with an electrochemical window of 1.5 V, preferably 2.0 V is required to achieve Pt dissolution. The added metal salt needed to have a higher decomposition potential than 1.5 V or should be a Pt salt.

**Keywords** Platinum · Electrodissolution · Ionic liquids ·  $\text{ZnCl}_2$ -EMIC ·  $\text{ZnCl}_2$ -ChCl

## 1 Introduction

Platinum group metals (especially Pt) play a key role in modern society, as they possess a range of unique chemical and physical properties. Pt is soft, ductile, and resistant to

oxidation and high temperature corrosion. Because of these properties it is highly applicable in a broad range of applications. Important applications beyond the well-known areas of chemical process catalysis and automotive emissions control include information technology (IT), consumer electronics, a variety of medical uses and sustainable energy production such as fuel cells, among others [1–5].

Given the need to expand almost all of these markets to meet the environmental and technological challenges of this century, the demand for Pt is expected to continuously grow [6]. However, the limited resources for Pt, however, pose a problem. One way to ensure adequate supplies is to increase exploration and extraction of geological deposits [5, 7, 8]. Increasing the efficiencies of the processes involved may offer some additional gains, but comprehensive recycling efforts are vital to keep up with the demand. As a result the growing demand for pure Pt metal and its alloys makes it necessary to develop efficient and environmentally friendly recycling processes. The recycling of Pt is a challenging and complicated process [9–15], which in a first step requires its dissolution. Pt is considered to be one of the “noblest” metals. Thus far, only the highly corrosive reagents like aqua regia ( $\text{HNO}_3/\text{HCl}$ ) [9, 10] or strong oxidative reagents like piranha acid ( $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ ) [11, 12] have been used for its dissolution.

Electrochemical dissolution in ionic liquids (IL's) is a possible solution to this challenge. They are defined as salts that melt below  $100^\circ\text{C}$ , typically consisting of an organic cation and a wide range of anions. These days IL's have received great interest because of their unique properties. The most important properties of IL electrolyte solutions are their extremely low volatility, a high electrochemical stability (Electrochemical windows  $> 2 \text{ V}$ ), and a relative good electric conductivity ( $1\text{--}10 \text{ mS cm}^{-1}$  at RT) [13, 14].

Huang and Chen [15] from the National Chung Hsing University in Taiwan demonstrated that significant

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electrodissolution of a large amount of Pt metal in the basic 1:3  $\text{ZnCl}_2$ –EMIC IL at a high dissolution rate is possible. They have also reported the recovery of pure Pt metal and the electrodeposition of Pt alloys.

The first purpose of the experiments described in this article was to understand the system used by Jing-Fang Huang and Hao-Yuan Chen and to develop a theory why Pt dissolution and deposition is possible in this electrolyte.

Our purpose is to build an in-depth theory about the dissolution mechanism for this IL electrolyte system. Once this mechanism has been revealed, new and cheaper systems can be developed.

## 2 Materials and methods

### 2.1 Chemicals

The various IL's were prepared by mixing the appropriate quantities of the components in a beaker, followed by heating (1–3 h) until a clear homogeneous solution was obtained. The syntheses took place under  $\text{N}_2$  atmosphere. The IL's studied are summarized in Table 1.

### 2.2 Experimental setup

All electrochemical experiments were accomplished with an Autolab PGSTAT30 Potentiostat/Galvanostat controlled by Nova 1.5 software. A three-electrode electrochemical cell was used for the experiments. The electrodes used for measuring the voltammetric scans were:

- Counter electrodes (CE)
  - ITO (geometric surface  $2.5 \text{ cm}^2$ )
  - Glassy carbon (GC, 3 mm  $\varnothing$ , Basi MF)
- Working electrodes (WE)
  - GC (3 mm  $\varnothing$ , Basi MF)
  - Pt (1.6 mm  $\varnothing$ , Basi MF)
- Quasi-reference electrodes (RE)

- Zn wire (99.9997 %, Alfa Aesar)

The ITO CE was fabricated by attaching (Circuitworks, Conductive Epoxy) a copper wire, as a contact, on an ITO-coated PET plate (Sigma Aldrich,  $8\text{--}12 \Omega \text{ sq}^{-1}$ ). The epoxy loses its adhesive and conductive properties above  $100^\circ\text{C}$ . This puts a restrain on the operation temperature for the use of this electrode.

All electrodes were cleaned before each experiment. The GC and Pt electrodes were polished with an aqueous slurry of 0.05 mm Al, and purified with deionized water and acetone. The Zn and ITO electrodes were cleaned with deionized water and acetone before use. Prior to measuring  $\text{N}_2$  was bubbled through the electrolyte for 30 min.

All cyclic voltammograms (CV's) were measured as three consecutive cycles. The scan rate was always 100 mV/s. For the linear sweep (LS) voltammograms a scan rate of 1 mV/s was used.

The chronoamperometric measurements were performed over different time lengths and with various electrodes:

- CE
  - Stainless steel (SS, geometric surface  $3 \text{ cm}^2$ )
  - ITO (geometric surface  $2.5 \text{ cm}^2$ )
  - Ti (geometric surface  $1.5 \text{ cm}^2$ )
- WE
  - Pt (geometric surface  $0.3 \text{ cm}^2$ )
- Quasi-RE
  - Zn wire (99.9997 %, Alfa Aesar)
  - Pt wire

The ITO and Ti CE's were fabricated by attaching (Circuitworks, Conductive Epoxy) a copper wire as contact on the chosen materials. Again the operation temperature was limited due to the epoxy's loss of adhesive and conductive properties at temperatures above  $100^\circ\text{C}$ . The Pt WE consisted of four Pt wires coiled together forming a wire like structure. The surface was estimated based on its geometric form. All the CE, except the ITO, were pre-polished with sandpaper 800 grit and 1,200 grit and all the electrodes were

**Table 1** Summary ionic liquids (IL's)

| IL                        | Component(s)   | Ratio (mol%) |
|---------------------------|--|--------------|
| $\text{ZnCl}_2$ –EMIC     | Zinc chloride (Technipur, Merck) + 1-ethyl-3-methylimidazolium chloride (>98 %, Iolitec) | 1:3          |
| EMIC                      | 1-Ethyl-3-methylimidazolium chloride (>98 %, Iolitec)                                    | Pure         |
| $\text{ZnCl}_2$ –ChCl     | Zinc chloride (Technipur, Merck) + choline chloride (exp DAB 10, FCC, Merck)             | 1:1          |
| Ethaline (Scionix)        | Ethylene glycol + choline chloride (exp DAB 10, FCC, Merck)                              | 2:1          |
| Reline (Scionix)          | Urea + choline chloride (exp DAB 10, FCC, Merck)   | 2:1          |
| $\text{ZnCl}_2$ –ethaline | Zinc chloride (Technipur, Merck) + ethaline (Scionix)                                    | 1:8.2        |
| $\text{ZnCl}_2$ –reline   | Zinc chloride (Technipur, Merck) + reline (Scionix)                                      | 1:9.4        |

rinsed with deionized water and acetone before use. The electrolyte was bubbled with  $N_2$  for 30 min before every measurement.

A Pt wire (WE) of known weight was anodized under controlled potential conditions. At the end of each experiment, the electrode was removed from the ionic liquid, cleaned with deionized water and acetone, dried in a furnace, and weighed again to determine the weight loss. An X-ray fluorescence analyzer was used to examine the composition of the electrodeposits. The Pt concentration in the electrolyte after dissolution was detected with inductively coupled plasma optical emission spectrometry element analysis (ICP-OES; Agilent type E730). The sample was decomposed with a mixture of  $H_2SO_4$  and  $HNO_3$  in a quartz beaker on a heating plate.  $H_2SO_4$  and  $HNO_3$  were evaporated and the residue was dissolved in 10 vol.% HCl solution before measurement. A calibration curve was prepared for the concentration range for 0–50  $mg\ L^{-1}$  with a QC of 25  $mg\ L^{-1}$  and scandium was used as an internal standard.

As all the ionic liquids were miscible in water, the residual ionic liquid on the electrodes was removed easily by rinsing with deionized water following each experiment.

### 3 Results and discussion

#### 3.1 Synthesis of IL's

The used IL's and their main properties are summarized in Table 2. The water content is extremely important due to its significant influence on a number of properties like the electrochemical window (EW) [16],  $T_m$  and the conductivity. Karl Fischer titrations were used to determine the water content (Table 3).

During the synthesis of  $ZnCl_2$ -ethaline and  $ZnCl_2$ -reline IL's vapor emerged from the liquids indicating an evaporation process. The dissolved  $ZnCl_2$  destroys the hydrogen-bonded anion complex of ethaline by complexing with a

$Cl^-$  anion. The hydrogen bonds are broken and ethylene glycol is present as a neutral molecule. A new ionic liquid is formed with Choline<sup>+</sup>, [2CholineCl]<sup>+</sup> cations and  $ZnCl_3^-$ ,  $Zn_2Cl_5^-$ ,  $Zn_3Cl_7^-$  anions, in which ethylene glycol is dissolved [17–19]. This results in a solution consisting of 2 IL's: Ethaline and an IL in which ethylene glycol is dissolved. During the synthesis the evaporation of ethylene glycol and water is seen at elevated temperatures (both ethylene glycol and water have a boiling point around 100 °C at 760 mmHg [20]).

The same principle is valid for the  $ZnCl_2$ -reline IL. The hydrogen bonds are broken by  $ZnCl_2$  and urea is present as a neutral molecule. An ionic liquid is formed with Choline<sup>+</sup>, [2CholineCl]<sup>+</sup> cations, and  $ZnCl_3^-$  anions in which urea is dissolved [17]. The only difference with the ethylene glycol system is that during the synthesis no evaporation occurred as urea melts and decomposes at 135 °C.

#### 3.2 $ZnCl_2$ -EMIC

##### 3.2.1 Electrochemical analyses

To understand the electrochemical behavior of the  $ZnCl_2$ -EMIC IL's, voltammograms were recorded with and without Pt in the system. The first measurements performed in the potential range between –3 and 3 V showed unstable results and the measurement could not be repeated. After a couple of experiments it was found that the Zn RE was covered by a black layer after every experiment, insulating the RE. It was observed that this layer only appeared during the cathodic polarization of the WE to potentials below  $\pm 1.25$  V. To solve this problem, voltammograms were measured from anodic to cathodic side and only to potentials of max. –1.0/–1.25 V.

Figure 1 shows CV's of the  $ZnCl_2$ -EMIC IL on a GC and Pt WE recorded according to the above described method with a scan rate of 100 mV/s at 120 °C. The potential limits for this IL correspond to the cathodic reduction of  $EMI^+$  at –0.5 V (peak V), and the anodic

**Table 2** Selected properties of the investigated IL's

| IL                 | Ratio (mol%) | $T_{syn.}$ (°C) | $T_m$ (°C) | Water content (%) |
|--------------------|--------------|-----------------|------------|-------------------|
| $ZnCl_2$ -EMIC     | 1:3          | 90              | 80         | 0.69              |
| EMIC               |              |                 | 80         | x                 |
| Ethaline           |              |                 | RT         | 2.13              |
| Reline             |              |                 | RT         | 1.05              |
| $ZnCl_2$ -ethaline | 1:8.2        | 120             | RT         | 3.24              |
| $ZnCl_2$ -reline   | 1:9.4        | 120             | RT         | 0.59              |
| $ZnCl_2$ -ChCl     | 1:1          | 160             | 80         | 0.33              |

**Table 3** Summary assigned peaks and assumed reactions

| Peak      | Assumed reactions  |
|-----------|--|
| I         | Formation Pt complexes<br>$Pt(s) + xCl^- \rightarrow [PtCl_x]^{y-} + ye^-$                             |
| II        | $2Cl^- \rightarrow Cl_2(g) + 2e^-$   |
| III + IV  | 2 Step reduction formed Pt complexes<br>$[PtCl_x]^{y-} \rightarrow [PtCl_x]^{(y-)-} \rightarrow Pt(s)$ |
| V + VII   | $Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$  |
| VI        | $EMI^+ + e^- \rightarrow EMI$  |
| VIII + IX | Oxidizing degradation products of EMI  |

oxidation of  $\text{Cl}^-$  at 2.4 V (peak II), resulting in an EW of approximately 2.9 V. This is in good agreement with the determined 3 V by Hsiu et al. [21] and Schubert et al. [22].

A comparison between both CV's shows three additional peaks on the Pt WE. Only one anodic peak indicating a Pt oxidation is observed around 2.25 V (peak I). No peak in the same potential range is observed at the GC WE. This behavior suggests that the electrochemical oxidation of Pt metal is a one-step reaction. On the cathodic scan, there are two cathodic peaks at 1.2 (peak III) and 1.0 V (peak IV), likely referring to a Pt reduction. These findings are in good agreement with the proposed mechanism of Huang and Chen [15]. They claim that at  $T$  above 80 °C Pt dissolves as a  $[\text{PtCl}_6]^{2-}$  complex and that the reduction follows a two-step mechanism from  $\text{Pt}^{4+}$  to  $\text{Pt}^{2+}$  followed by the reduction to metallic Pt. Two additional anodic peaks (VI and VII) appear in both CV's. These peaks can be assigned to the oxidation of degradation products formed during the cathodic cycle.

The LS voltammograms of the anodic polarization were measured to take a closer look at the dissolution of Pt metal. Figure 2 shows the LS's of the 1:3  $\text{ZnCl}_2$ -EMIC IL recorded on a GC and Pt WE at a scan rate of 1  $\text{mV s}^{-1}$  at 120 °C.

From the previous proposed reaction mechanism it can be concluded that Pt oxidation was characterised by a peak starting around 2.0 V. Chronoamperometric measurements were performed on a potential above and below 2.0 V to proof that this reaction is indeed the dissolution of Pt.

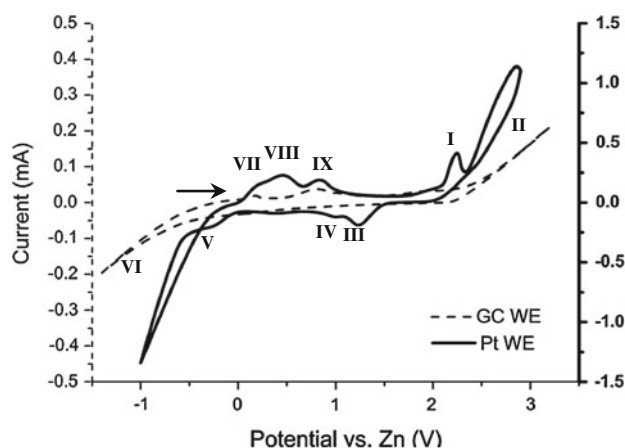
### 3.2.2 Chronoamperometric anodic dissolution of Pt

Based on the preceding voltammograms (Figs. 1, 2), we assumed that Pt dissolves at potentials higher than  $\pm 2$  V. The release of  $\text{Cl}_2$  gas around 2.4 V is an indication for the

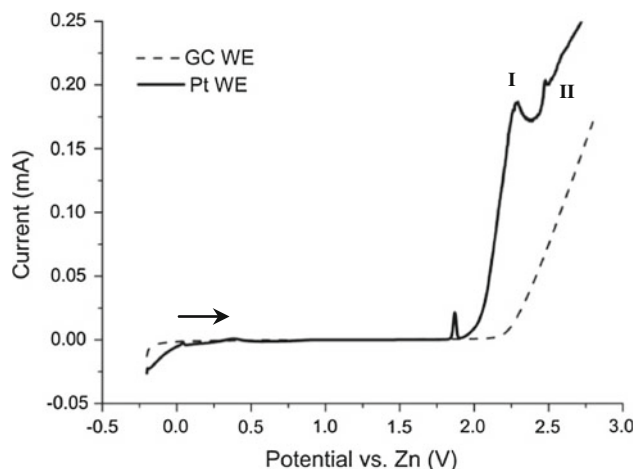
decomposition of the electrolyte and must be avoided. This implies that the applied potential to dissolve Pt must be chosen above 2 and below 2.4 V. This is confirmed by chronoamperometric measurements below 2.0 V where no dissolution of Pt could be observed.

Figure 3 shows the current/time transients of a chronoamperometric anodic dissolution of a Pt electrode in the  $\text{ZnCl}_2$ -EMIC IL. A potential of 2.1 V is applied for 8 h. Preparatory conditioning of the electrolyte was done by applying 2.1 V for 50 min. During this time, Pt ions were brought into solution and a Zn-Pt alloy was deposited on the cathode. As shown in Fig. 3, the current increases quickly at an early stage (first 200 s) followed by a steady decline because of the decrease in size of the WE. An average current of approximately 0.0035 A was reached during the experiment resembling a current density of  $116.67 \text{ A m}^{-2}$ . A weight loss of 0.0492 g occurred, leading to a dissolution rate of  $192.2 \text{ g m}^{-2} \text{ h}^{-1}$  ( $0.985 \text{ mol m}^{-2} \text{ h}^{-1}$ ). The current efficiency for the dissolution was calculated to be 99 %, assuming a  $\text{Pt}^{4+}$  valence. The high dissolution efficiency and the absence of gas formation at the anode indicated that no  $\text{Cl}_2$  was produced during the experiment and thus no decomposition of the electrolyte occurred. Afterward, a Pt concentration of 39 ppm was measured in solution by ICP-MS elemental analysis, and a Pt-Zn (4:96 %) deposition was detected at the cathode. The Zn deposition can be avoided by adding Pt salt to the starting electrolyte. Without adding Pt salt Zn will always be co-deposited due to the extremely low Pt concentrations in the electrolyte.

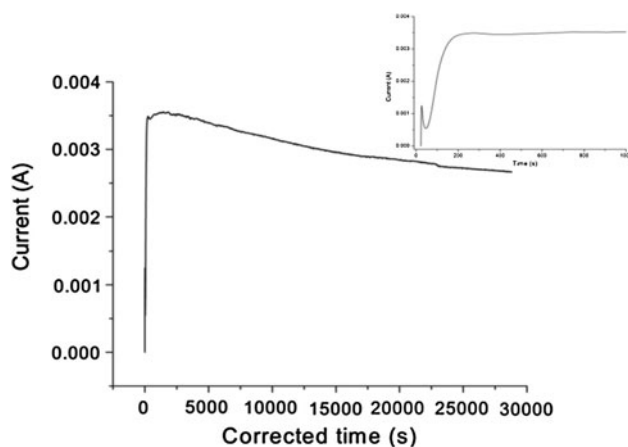
The experiment confirmed that the basic 1:3  $\text{ZnCl}_2$ -EMIC IL is indeed an excellent medium for the electro-dissolution of large amounts of Pt metal at a high dissolution rate. The drawback, however, is that it is a quite expensive system. To overcome this problem, less expensive systems were investigated.



**Fig. 1** CV's of the 1:3  $\text{ZnCl}_2$ -EMIC IL recorded on a GC (dashed line) and Pt (solid line) WE at the scan rate of 100  $\text{mV s}^{-1}$  at 120 °C (ITO CE dashed line, GC CE solid line) with three coinciding cycles



**Fig. 2** LS's of the 1:3  $\text{ZnCl}_2$ -EMIC IL recorded on a GC (dashed line) and Pt (solid line) WE at the scan rate of 1  $\text{mV/s}$  at 120 °C (ITO CE dashed line, GC CE solid line)



**Fig. 3** Current/time transient at  $E = 2.1$  V in 1:3  $\text{ZnCl}_2$ -EMIC IL at  $120^\circ\text{C}$  with a Pt WE (Stainless Steel CE) Upper inset magnification of the current/time transients in the 0–1,000 s range

1:3  $\text{ZnCl}_2$ -EMIC belongs to the eutectic-based IL's, and more specific to type 1. Ionic liquids have been classified by their anionic species into so-called first and second generation liquids, where the first generation IL's have complex anions formed between a Lewis basic anion and a Lewis acid metal salt or a Brønsted acid hydrogen bond donor. These are, in effect, eutectic mixtures of the two components and are therefore called eutectic-based IL's. Second generation ionic liquids have discrete anions. The eutectic-based systems can be expressed in terms of the general formula  $\text{Cat}^+\text{X}^-\cdot z\text{Y}$ , where  $\text{Cat}^+$  is basically any ammonium, phosphonium, or sulfonium cation,  $\text{X}^-$  is generally a halide ion (usually  $\text{Cl}^-$ ). They are based on an equilibria set up between  $\text{X}^-$  and a Lewis or Brønsted acid Y,  $z$  refers to the number of Y molecules which complex  $\text{X}^-$ . The IL's described can be subdivided into three types depending on the nature of the complexing agent used [23].

Type 1:  $\text{Y} = \text{MCl}_x$ ,  $\text{M} = \text{Zn, Sn, Fe, Al, Ga, In}$

Type 2:  $\text{Y} = \text{MCl}_x \cdot y\text{H}_2\text{O}$ ,  $\text{M} = \text{Cr, Co, Cu, Ni, Fe}$

Type 3:  $\text{Y} = \text{RZ}$ ,  $\text{Z} = \text{CONH}_2, \text{COOH, OH}$

To make Pt dissolution industrial feasible, less expensive systems were evaluated. To dissolve Pt metal as a  $[\text{PtCl}_x]^{y-}$  complex, only  $\text{Cl}^-$  anion containing IL's were chosen. Tests were performed to assess the dissolution of Pt and to develop a solid theory regarding the dissolution potential of different electrolyte types.

### 3.3 Alternative electrolyte systems

A summary of the electrolytes tested and the potential to dissolve Pt is given in Table 4. All electrolytes were analyzed by cyclic and linear sweep voltammetry experiments (Table 5)

Assessment of the first generation type 3 (reline, ethaline) showed that they are not able to dissolve Pt. The main

difference between the  $\text{ZnCl}_2$ -EMIC and the so far tested IL's is the lack of  $\text{ZnCl}_2$  in the latter system. The incapability of Pt dissolution in EMIC, a second generation IL, proves that a metal chloride has an important role in the dissolution of Pt. Therefore,  $\text{ZnCl}_2$  was added to the ethaline and reline.

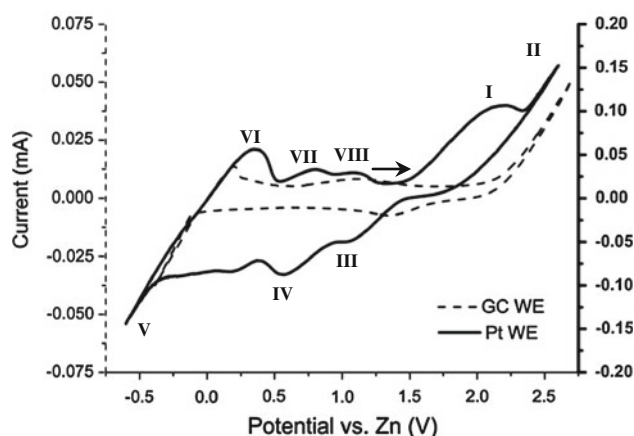
However, the addition of  $\text{ZnCl}_2$  (0.5 M) to the systems did not change the outcome. The conclusion could be that the addition of  $\text{ZnCl}_2$  (0.5 M) partly destroyed the hydrogen-bonded anion complex forming a new ionic liquid with  $\text{Choline}^+$ ,  $[\text{2CholineCl}]^+$  cations and  $\text{ZnCl}_3^-$ ,  $\text{Zn}_2\text{Cl}_5^-$ ,  $\text{Zn}_3\text{Cl}_7^-$  anions in which Urea or Ethylene glycol were dissolved [17]. Instead of the  $\text{ZnCl}_2$ -ethaline/ $\text{ZnCl}_2$ -reline ionic liquid, most probably a solution consisting of an IL containing ethaline or reline and an IL with  $\text{Choline}^+$  cations and  $\text{ZnCl}^-$  anions was produced in which ethylene glycol or urea were dissolved.

The type 2 eutectic-based IL's were not tested. These IL's contain hydration water. Water normally limits the EW but the role of the hydration water molecules is still largely unknown. The authors [24–26] claim that the hydration water does not act in the same way as bulk water and that the EW is rather limited by the metallic species reduction than the water-related reduction processes. However, it is the chromium system which has been published so far.

Following these results a  $\text{ZnCl}_2$ -ChCl IL was tested, showing positive results regarding the dissolution of Pt.

### 3.4 $\text{ZnCl}_2$ -ChCl IL

The 1:1  $\text{ZnCl}_2$ -ChCl IL is a type 1 eutectic-based IL like 1:3  $\text{ZnCl}_2$ -EMIC but less expensive. Due to the positive Pt dissolution assessment, a full analysis of this system was made.



**Fig. 4** CV's of the 1:1  $\text{ZnCl}_2$ -ChCl IL recorded on a GC (dashed line) and Pt (solid line) WE at the scan rate of  $100\text{ mV s}^{-1}$  at  $100^\circ\text{C}$  (ITO CE dashed line, GC CE solid line) with three coinciding cycles



**Table 4** Alternative electrolytes

| IL                          | EW (V) | <i>T</i> (°C) | Pt diss. | <i>J</i> (A m <sup>−2</sup> ) | Max. <i>η</i> (%) |
|-----------------------------|--------|---------------|----------|-------------------------------|-------------------|
| EMIC                        | 2.1    | 100           | No       |                               |                   |
| Ethaline                    | 1.9    | 100           | No       |                               |                   |
| Reline                      | 2.0    | 100           | No       |                               |                   |
| ZnCl <sub>2</sub> –ethaline | 2.2    | 100           | No       |                               |                   |
| ZnCl <sub>2</sub> –reline   | 2.2    | 100           | No       |                               |                   |
| ZnCl <sub>2</sub> –ChCl     | 2.9    | 100           | Yes      | 5.5                           | 96                |

**Table 5** Summary assigned peaks and assumed reactions

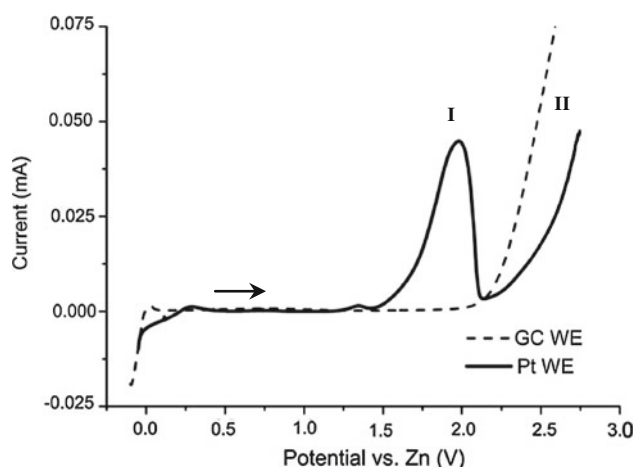
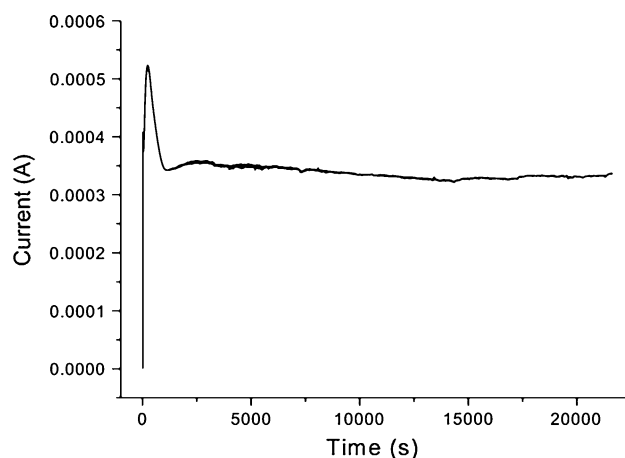
| Peak       | Assumed reactions  |
|------------|--|
| I          | Formation Pt complexes<br>$\text{Pt(s)} \rightarrow [\text{PtCl}_2]^{2-}$  |
| II         | $2\text{Cl}^- \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$   |
| III + IV   | 2 Step reduction formed Pt complexes<br>$[\text{PtCl}_x]^{y-} \rightarrow [\text{PtCl}_2]^{2-} \rightarrow \text{Pt(s)}$ |
| V + VI     | $\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn(s)}$   |
| VII + VIII | Degradation products of choline  |

### 3.4.1 Electrochemical analysis

Figure 4 shows the CV's of the 1:1 ZnCl<sub>2</sub>–ChCl IL recorded on a GC and Pt WE at a scan rate of 100 mV/s at 100 °C. The potential limits for this IL correspond to the cathodic reduction of Zn at −0.1 V (peak V), and anodic oxidation of Cl<sup>−</sup> at 2.1 V (peak II), giving an EW of approximately 2.2 V. This is in good agreement with the determined 2 V by Abbott et al. [27].

As shown in Fig. 4, three additional peaks arise in the CV recorded on the Pt WE in comparison with the one recorded on the GC WE. Only one anodic peak corresponding to Pt oxidation is observed around 2.3 V (peak I). Again no peak is observed, around the same voltage, on the GC WE. This behavior suggests that the electrochemical oxidation of Pt metal is a one-step reaction as concluded previously. On the cathodic scan, there are two cathodic peaks around 1.0 (peak III) and 0.55 V (peak IV), corresponding to a Pt reduction. Three additional anodic peaks appear in both the CV's. These peaks were due to the oxidation of degradation products formed during cathodic cycle.

The linear sweep voltammogram (LS) of the anodic polarization at the scan rate of 1 mV/s at 100 °C is shown in Fig. 5.

**Fig. 5** LS's of the 1:1 ZnCl<sub>2</sub>–ChCl IL recorded on a GC (dashed line) and Pt (solid line) WE at the scan rate of 1 mV s<sup>−1</sup> at 100 °C (ITO CE)**Fig. 6** The current/time transient from the chronoamperometric experiment at *E* = 2.1 V for the Pt anodic dissolution process in 1:1 ZnCl<sub>2</sub>–ChCl IL at 100 °C (ITO CE)

### 3.4.2 Chronoamperometric anodic dissolution of Pt

Based on the preceding voltammograms (Figs. 4, 5), it is known that Pt dissolves at voltages above 1.7 V. The release of Cl<sub>2</sub> gas around 2.1 V must be avoided. Dissolution experiments were conducted with a chronoamperometric setup on Pt WE's at potentials between 1.7 and 2.1 V.

Figure 6 shows the current/time transients from one of these dissolutions in the 1:1 ZnCl<sub>2</sub>–ChCl IL. A potential of 2.1 V is applied for 6 h. Pt ions were previously brought into solution by the same conditioning experiment already performed in the ZnCl<sub>2</sub>–EMIC IL. An ITO CE was chosen instead of a SS CE, due to the fact that the SS is etched in the 1:1 ZnCl<sub>2</sub>–ChCl IL, introducing Fe ions into the electrolyte.

During the chronoamperometric experiment an average current of approximately  $2.7\text{E}^{-4}$  A was reached, resembling a current density of  $9\text{ A m}^{-2}$ . A weight loss of  $0.0005\text{ g}$  occurred, leading to a dissolution rate of  $2.6\text{ g m}^{-2}\text{ h}^{-1}$  ( $0.013\text{ mol m}^{-2}\text{ h}^{-1}$ ) and a dissolution efficiency of  $15\%$ . The dissolution efficiency was calculated assuming that the Pt dissolved as  $\text{Pt}^{4+}$ . During the experiment  $\text{Cl}_2$  gas release was observed at the WE explaining the low dissolution efficiency.

After the experiment Pt was detected on the cathode in the form of dendrites.

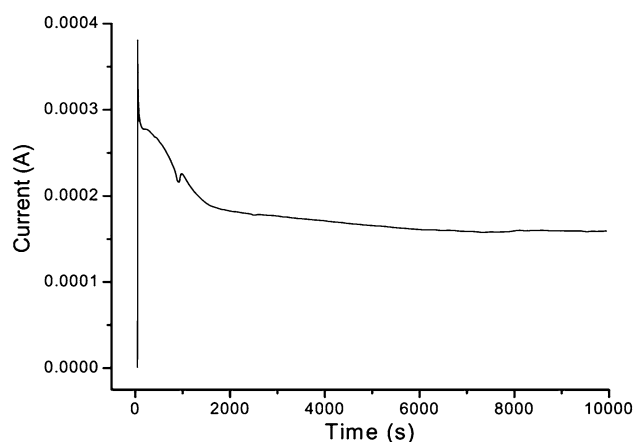
To increase the dissolution efficiency a lower potential ( $2.0\text{ V}$ ) was applied to avoid  $\text{Cl}_2$  gas release and the experiment was repeated with a Ti CE for  $2\text{ h } 45\text{ min}$  (Fig. 7). An average current of approximately  $1.66\text{E}^{-4}$  A was reached, resembling a current density of  $5.5\text{ A/m}^2$ , and a weight loss of  $0.0008\text{ g}$  occurred, leading to a dissolution rate of  $9.090\text{ g m}^{-2}\text{ h}^{-1}$  ( $0.0047\text{ mol m}^{-2}\text{ h}^{-1}$ ). A dissolution efficiency of  $96\%$  was calculated. The very high dissolution efficiency was an indication that  $\text{Cl}_2$  gas release was avoided at the chosen potential.

Due to a small CE surface a Zn layer with minor traces of Pt was produced on the Ti cathode and a Pt powder in the electrolyte, both confirmed by energy-dispersive X-ray spectroscopy (EDS) on the cathode (Fig. 8) and the filtered powder (Whatmann, Grade 589/2).

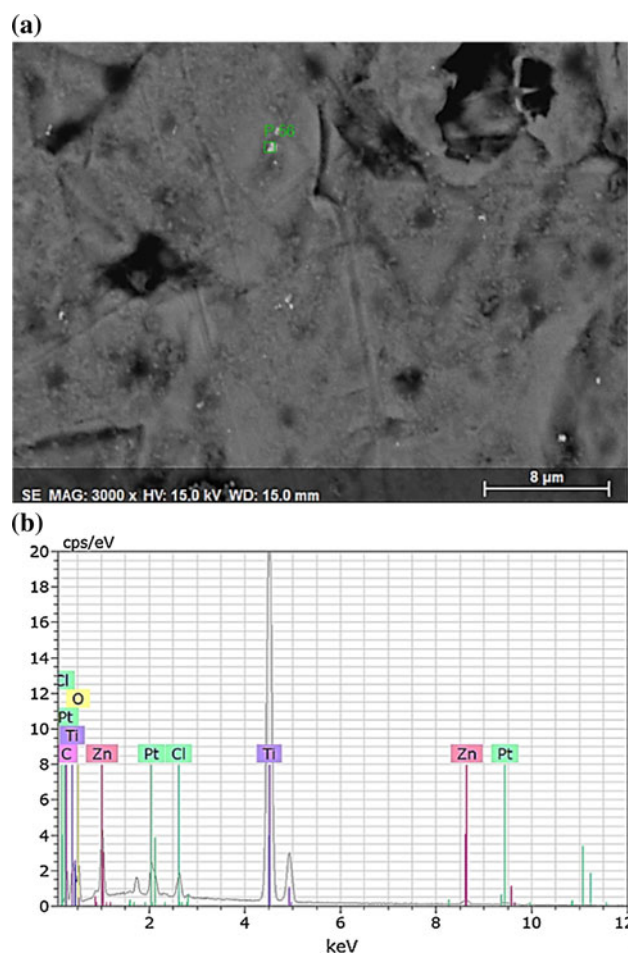
The possibility to dissolve Pt in  $\text{ZnCl}_2\text{--ChCl}$  indicates that the dissolution can be achieved in a type 1 eutectic IL with the addition of a metal chloride. From the voltammograms measured for the  $1:3\text{ ZnCl}_2\text{--EMIC}$  (Figs. 1, 2) and the  $1:1\text{ ZnCl}_2\text{--ChCl}$  (Figs. 4, 5) it was concluded that the EW of the IL's needs to be at least  $1.5\text{ V}$  to dissolve and deposit Pt. So the metal salt added needs to have a higher decomposition potential than  $1.5\text{ V}$ , in our case  $\text{ZnCl}_2$  or a less noble salt. As an alternative a Pt salt could be added directly to form an IL.

#### 4 Conclusions

The electrochemical dissolution of Pt in several ionic liquids (IL's) was studied. Different IL's were tested assessing their potential to dissolve Pt by evaluating the dissolution rate and the current efficiency. First, according to Huang and Chen [15], it was reviewed that the basic  $1:3\text{ ZnCl}_2\text{--}1\text{-ethyl-3-methylimidazolium chloride}$  ionic liquid ( $\text{ZnCl}_2\text{--EMIC}$  IL) served as a solvent system for the electrodisolution of large amounts of Pt metal. The next objective was to find more “industrial, less expensive” systems that show at last the same result. The electrochemical behavior of the IL's was studied by voltammetry and chronoamperometry. The main focus lies on Cl containing IL's of both classes: First generation, eutectic-based



**Fig. 7** The current/time transient from the chronoamperometric experiment at  $E = 2.0\text{ V}$  for the Pt anodic dissolution process in  $1:1\text{ ZnCl}_2\text{--ChCl}$  IL at  $100^\circ\text{C}$ . (Ti CE)



**Fig. 8** Back scattered electron image (a) and corresponding EDS spectra (b) of the deposition on the Ti CE

IL's and second generation, IL's with discrete anions (e.g., EMIC). A further distinction was made between the different types of eutectic-based IL's: Type 1 metal salts (e.g.,  $\text{ZnCl}_2\text{--ChCl}$ ), type 2 hydrated metal salts (e.g.,

ZnCl<sub>2</sub>; 2H<sub>2</sub>O–ChCl), and type 3 hydrogen bond donors (e.g., reline, ethaline).

Pt dissolution was only possible in the type 1 eutectic-based IL's (ZnCl<sub>2</sub>–EMIC and ZnCl<sub>2</sub>–ChCl). These IL's contained an excess in Cl<sup>−</sup> anions due to the metal chloride salts added. At adjusted potentials, these metal salts donated their Cl<sup>−</sup> anions to the Pt metal. The Pt dissolved by forming a [PtCl<sub>x</sub>]<sup>y−</sup> complex in the electrolyte.

Comparing the dissolution rates reveals that the dissolution of Pt in the 1:3 ZnCl<sub>2</sub>–EMIC IL is with 192.2 g m<sup>−2</sup> h<sup>−1</sup> (0.985 mol m<sup>−2</sup> h<sup>−1</sup>) a lot faster than in the 1:1 ZnCl<sub>2</sub>–ChCl IL with 9.090 g m<sup>−2</sup> h<sup>−1</sup> (0.0047 mol m<sup>−2</sup> h<sup>−1</sup>). The price of the EMIC being €740/kg higher than for the ChCl makes it industrially less interesting. All other types of IL's tested did not show the Pt dissolution. This demonstrates that type 1 Eutectic-based IL's can be successfully used if the EW of the IL's is at least 1.5 V. The metal salt added should have a higher decomposition potential than 1.5 V, in our case ZnCl<sub>2</sub> or a less noble salt.

Further investigations will be executed in type 1 IL's, focusing on the optimization of the ZnCl<sub>2</sub>–ChCl systems to improve the dissolution rate and the max. J through addition of Pt salt, increase of *T*, and appliance of stirring. It might also be interesting to investigate if a type 1 IL can be formed directly with a Pt salt.

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